

Absorption of Carbon Dioxide in Sodium Carbonate-Bicarbonate Solutions

I. Equilibrium in System Carbon Dioxide-Sodium Carbonate-Sodium Bicarbonate-Water

II. Rate of Absorption

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I. Equilibrium in System Carbon Dioxide-Sodium Carbonate-Sodium Bicarbonate-Water

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Experiments have been performed to determine the equilibrium relationship between temperature, partial pressure of carbon dioxide in the gas phase, and chemical composition of the liquid, for a range of conditions approximating those encountered in the absorption process as operated in practice. The results of these experiments have been correlated with the work of McCoy and Smith (3) and an empirical equation,

$$\frac{X^2 C^{1.29}}{SP(1 - X)(185 - t)} = 10$$

representing the equilibrium relationship between temperature, partial pressure of carbon dioxide in the gas, and chemical composition of the liquid, has been developed.

CARBON dioxide of high purity is obtained from flue gases (or other gases containing carbon dioxide) by a process in which the carbon dioxide is separated from the other constituents of the flue gas by means of a liquid absorption medium which preferentially absorbs the carbon dioxide. An aqueous sodium carbonate-bicarbonate solu-

tion is a liquid absorption medium commonly employed. Accurate design of absorption equipment for this process is facilitated by a knowledge of the relationships between the various conditions under which the absorption is to take place and (1) the equilibrium which tends to be established between the carbon dioxide concentration in the gas and the concentration of carbonate and bicarbonate in the liquid, and (2) the rate at which carbon dioxide tends to be absorbed from the gas by the liquid. The present article treats the question of equilibrium; another article will consider the question of absorption rate.

The reversible reaction



is utilized in the absorption process for producing essentially pure carbon dioxide from flue gas (which contains approximately 18 per cent carbon dioxide, 80 per cent nitrogen, and the balance carbon monoxide, oxygen, sulfur compounds, and organic matter). The process involves two stages. In the first stage, the flue gas is exposed to an aqueous solution containing sodium carbonate under conditions which favor the formation of sodium bicarbonate according to Equation 1; carbon dioxide is removed from the flue gas and is stored in the liquid as sodium bicarbonate. In the second stage, the liquid is removed from contact with the flue gas and is subjected to conditions which favor the decomposition of sodium bicarbonate with the formation of sodium carbonate, carbon dioxide, and water; the carbon dioxide is evolved from the solution accompanied only by water vapor, which is easily removed by condensation. To the designer of equipment for absorbing carbon dioxide in sodium carbonate-bicarbonate solutions, it is of considerable interest to know just where the reaction represented by Equation 1 will balance for the different conditions which are likely to be encountered when the equipment is put into operation.

WORK OF EARLIER INVESTIGATORS

The system under consideration consists of a gas phase and a liquid phase; it is a two-phase system containing three components. Application of the familiar phase rule of Gibbs reveals that there are three degrees of freedom; it follows that, when the system is at equilibrium, the ratio of sodium bicarbonate to sodium carbonate, the temperature, the partial pressure of carbon dioxide in the gas, the total sodium concentration in the liquid, and all other variables are fixed if any three independent variables are fixed. An equation showing the equilibrium relationship between certain variables has been developed from theoretical considerations by McCoy and Smith (3):

$$\frac{2 X^2 C}{SP (1 - X)} = M \quad (2)$$

Experimental work by McCoy and Smith and by Sieverts and Fritzsche (5)¹ has indicated that M (of Equation 2) is independent of P and X , but that it varies with temperature and with the total sodium concentration. The practical significance of these experimental findings may be summarized as follows:

1. At a particular temperature and for a particular total sodium concentration, a single value of M will permit the calculation of the corresponding equilibrium values, X and P .

2. Every new set of conditions in which either temperature or total sodium concentration takes on a new value requires a new value of M .

If reliable values of M for the entire range of temperature and sodium concentration which it is desired to consider were available, Equation 2 would furnish all the desired information concerning equilibrium. Unfortunately, only a few values of M have been recorded, and it has been necessary to make some new determinations. This paper concerns itself with presenting the previously determined values of M , telling how the authors determined some additional values of M , and showing how the previously determined values and the authors' values may be used to modify Equation 2 so that it becomes applicable for any sodium concentration between 0.5 and 2.0 normal and for any temperature from 20° to 70° C.

McCoy and Smith have reported values of M at 25° C. for sodium carbonate-bicarbonate solutions 0.1, 0.3, and 1.0 normal in sodium, and for partial pressures of carbon dioxide varying over a considerable range. The values of M reported by these investigators are given in Table I. A search of the literature has failed to reveal any other values of M for conditions within the scope of the present work. [The work of Walker, Bray, and Johnston (6) is limited to partial pressures of carbon dioxide which are relatively low (of the order of 1 to 3 mm. of mercury) and far removed from the range of partial pressures (about 30 to 150 mm. of mercury) considered in the present investigation.]

EXPERIMENTS TO DETERMINE VALUES OF M

The almost complete lack of published information concerning the value of M for temperatures above 25° C. and for sodium concentrations greater than 1.0 normal led the authors to undertake some experimental work which aimed to supply values of M for this range of conditions.

The experimental determination of M for a particular temperature and a particular sodium normality involved.

- (1) establishing equilibrium, at the desired temperature,

¹ Sieverts and Fritzsche worked with potassium carbonate-bicarbonate solutions instead of the corresponding sodium carbonate-bicarbonate solutions, but, since the theoretical considerations upon which Equation 2 was developed apply as well for the potassium as for the sodium solutions, the work of Sieverts and Fritzsche furnishes experimental verification of Equation 2.

between a liquid phase having the desired sodium normality and a gas phase having a known partial pressure of carbon dioxide; and (2) analyzing the liquid phase to determine the equilibrium concentrations of carbonate and bicarbonate. This procedure furnished sufficient information (since it provided data which gave values of t , X , C , S , and P) to permit calculation of the desired value of M by means of Equation 2. The experimental work was planned and carried out with the thought in mind that the degree of confidence which might be placed in the results obtained was likely to depend upon how nearly the true equilibrium conditions were approached and how accurate the analysis of the liquid phase happened to be.

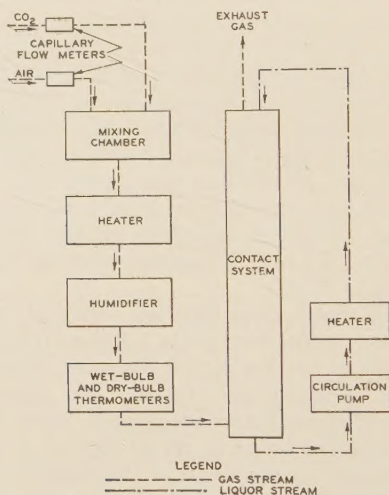


FIGURE 1. FLOW SHEET OF APPARATUS

TABLE I. VALUES OF M REPORTED BY MCCOY AND SMITH^a

C	t	p	M
0.1	25	12 — 57	5300 $\pm$ 400
0.3	25	24 — 34	4460 $\pm$ 100
1.0	25	33 — 128	3120 $\pm$ 200

^a Several determinations of M for different values of p , over the range indicated in column 3, were made while C and t were held constant at the values indicated in columns 1 and 2; column 4 shows the mean of these several determinations, plus or minus the deviation from the mean of the most divergent value.

The general scheme of the apparatus is shown in Figure 1.

Air was supplied from the laboratory compressed-air line. Carbon dioxide was supplied from tanks of the commercial liquid product. Use of suitable reducing valves and capillary flowmeters permitted the ratio of carbon dioxide to air to be regulated as desired. A heater and a humidifier regulated the temperature of the air and insured its saturation with water vapor. In the contact system, which consisted of a tower of the wetted-wall type similar to the towers described by Haslam, Hershey, and Keen (2), and by Greenewalt (1), the gas stream came into contact with the liquor stream. The gas, after making a single pass

through the contact system, was exhausted to the atmosphere. The liquor stream flowed in a closed circuit, being pumped through the contact system over and over again by the circulation pump. The liquor stream was kept at the desired temperature by means of a heater.

The process by which gas and liquor were brought into equilibrium was a continuous process with respect to the gas phase but a batch process as far as the liquid phase was concerned. The composition of the gas stream did not change during a given run. The composition of the liquor stream, on the other hand, did change during a run, tending to assume that ratio of carbonate to bicarbonate which would be in equilibrium with the gas stream. Periodic analysis of the liquor stream indicated the way in which its composition was changing. For a particular temperature, a particular sodium normality, and a particular gas composition, at least two runs, one in which the liquor contained more than the equilibrium concentration of bicarbonate at the start and another in which the liquor contained

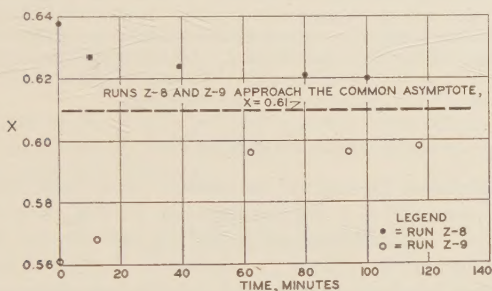


FIGURE 2. CHANGE OF LIQUOR COMPOSITION WITH TIME

less than the equilibrium concentration of bicarbonate at the start, were made. When liquor containing more than the equilibrium concentration of bicarbonate was used, decomposition of bicarbonate occurred, carbon dioxide was evolved, and equilibrium was approached from the right-hand side of Equation 1; when liquor containing less than the equilibrium concentration of bicarbonate was used, carbon dioxide was absorbed, bicarbonate was formed, and equilibrium was approached from the left side. By approaching from both sides, it was possible to locate the equilibrium conditions within close limits. An approach from one side only might lead one to mistake conditions where change of composition was slow for the true equilibrium conditions. A standard procedure was followed in these experiments:

The gas stream was adjusted with respect to composition, temperature, and humidity. Carbon dioxide and air were mixed in the desired proportions by adjusting the valves on the feed lines. The ratio of carbon dioxide to air was checked by analyzing the gas mixture for carbon dioxide content. The temperature

and humidity determinations were made by means of wet-bulb and dry-bulb thermometers. After being adjusted, the gas stream was by-passed around the contact system until the liquor stream had been adjusted. Approximately 1600 cc. of a solution of the desired sodium concentration, either 1.0 or 2.0 normal, and having a carbonate-bicarbonate ratio somewhat removed from the equilibrium ratio, was prepared and measured into the contact system. A heater (Figure 1) was used to bring the temperature of the liquor stream to the desired point. When both streams had been adjusted satisfactorily, the gas stream was switched from the by-pass to the contact system, and the initial sample of the liquor was withdrawn for analysis. The duration of a run was usually about 2 hours, during which time liquor samples were withdrawn about every half-hour. The liquor samples were analyzed to determine the total sodium concentration and the fraction of the sodium in the form of the bicarbonate. The temperature of both streams and the composition of the gas stream remained constant throughout a given run. Total sodium concentration was determined by the familiar titration with standard acid, using methyl orange as indicator. Carbonate and bicarbonate concentrations were determined by a modification of the Winkler method; a measured volume of standard barium hydroxide solution, more than the amount required to convert all the bicarbonate to carbonate, was added along with sufficient barium chloride solution to insure precipitation of all the carbonate; the excess of base, determined by back-titrating with standard acid (indicator was phenolphthalein) an aliquot of the clear liquor above the precipitated barium carbonate, indicated how much base had been used by the bicarbonate and thus gave a measure of the bicarbonate concentration.

DATA FROM EXPERIMENTAL WORK

For solutions 1.0 normal in sodium, runs were made at 25°, 45°, and 63° C.; for solutions 2.0 normal, runs at 45° and 63° C. Summarized data for the two runs at 63° C. and 1.0 normal in sodium (presented in Tables II and III and Figure 2) show the type of information obtained.

TABLE II. CONDITIONS FOR RUNS Z-8 AND Z-9

	Z-8	Z-9
Sodium normality	0.946	0.963
Temperature, ° C.	63 ± 2	63 ± 2
Total pressure, mm. Hg	752	752
CO ₂ in gas (dry basis), %	6.44	6.44

TABLE III. FRACTION OF SODIUM AS BICARBONATE *vs.* TIME FOR RUNS Z-8 AND Z-9

RUN Z-8 Time		RUN Z-9 Time	
Minutes	X	Minutes	X
0	0.638	0	0.561
10	0.627	12	0.568
39	0.624	62	0.596
80	0.621	94	0.596
100	0.620	117	0.598

Figure 2 presents, in graphical form, the information tabulated in Table III, and illustrates how the chemical composition of the liquor changed with time to approach the equilibrium composition as an asymptote. Figure 2 shows why it is important to approach equilibrium conditions from both sides; a common asymptote for two curves can be located

with greater accuracy and confidence when the asymptote lies between the two curves than when both curves are on the same side of the asymptote.

Tables II and III and Figure 2 furnish the information required for obtaining values of X , C , S , and P .

X is the fraction of the total sodium in the liquor which is in the form of sodium bicarbonate. The value of X to be substituted in Equation 2 is the equilibrium value (the value which X approaches as the time of contact between gas and liquor approaches infinity). For runs Z-8 and Z-9 the equilibrium value of X was 0.61, as may be seen from Table III or Figure 2.

C is the sodium normality of the solution. C is obtained directly from the liquor analysis. The difference in sodium concentration for runs Z-8 and Z-9 is small, and a value between the two (0.95) may be taken as the value of C to be substituted in Equation 2.

S is the solubility of carbon dioxide in water at the temperature of the experiment. The value of S at 63° C. is 0.0151 (Seidell, 4).

P is the partial pressure of carbon dioxide expressed in atmospheres. P is computed from the total pressure on the system and the carbon dioxide content of the gas stream. The total pressure on the system, for runs Z-8 and Z-9, was 752 mm. Subtraction of 171 mm. (the vapor pressure of water at 63° C.) leaves a dry pressure of 581 mm. Since the carbon dioxide content of the gas stream was 6.44 per cent (dry basis), the partial pressure of carbon dioxide is $(0.0644)(581/760) = 0.0429$ atmospheres = P .

A value of M (2440) for 63° C. and a sodium normality of 0.95 may be obtained by substituting the above values of X , C , S , and P in Equation 2.

$$M = \frac{(2)(0.61)^2(0.95)}{(0.0151)(0.0492)(0.39)} = 2440$$

Similar treatment of the data for other runs resulted in values of M for other conditions of temperature and sodium concentration. Table IV shows the values of M obtained in this work and, in addition, reëxhibits certain values of M reported by McCoy and Smith.

TABLE IV. VALUES OF MCCOY COEFFICIENT, M

C	t	M	
		Exptl.	Equation 6
0.3	25	(4460) ^a	4550
1.0	25	(3120)	3200
1.0	25	3150	3200
1.0	45	2840	2800
0.95	63	2440	2470
2.0	25	(2660) ^b	2620
1.96	45	2335	2300
1.95	63	1910	2010

^a Values in parentheses reported by McCoy and Smith.

^b Obtained by extrapolating values reported by McCoy and Smith.

CORRELATION OF DATA BY EMPIRICAL EQUATION

The values of M , which are presented in Table IV, may be used in Equation 2 to calculate equilibrium relationships for certain particular temperatures and sodium concentra-

tions. To permit the general application of Equation 2 for any temperature between 20° and 70° C. and for any sodium normality between 0.5 and 2.0 normal, other values of M may be obtained by interpolation or extrapolation. Graphical interpolation and extrapolation on a chart showing M vs. C , or M vs. T will furnish the desired values of M , but the alternative method of using an empirical equation may prove more convenient.

The authors have developed an empirical equation (Equation 6) which represents the available experimental values of M with a fair degree of accuracy. It was found that when the logarithm of M was plotted against the logarithm of C , three parallel straight lines, one for each of the three temperatures, could be drawn through the points. The equations of these lines were:

$$\text{at } 25^{\circ} \text{ C.:} \quad M = 3150 C^{-0.29} \quad (3a)$$

$$\text{at } 45^{\circ} \text{ C.:} \quad M = 2840 C^{-0.29} \quad (3b)$$

$$\text{at } 63^{\circ} \text{ C.:} \quad M = 2370 C^{-0.29} \quad (3c)$$

The general form of these equations is:

$$\text{at } t^{\circ} \text{ C.:} \quad M = B C^{-0.29} \quad (4)$$

where B = a numerical coefficient

When the numerical coefficient, B , for each of the three equations, 3a, 3b, and 3c, was plotted against the corresponding temperature, t , three points which lay nearly on a straight line were obtained. The equation of this line was:

$$B = 20 (185 - t) \quad (5)$$

Substitution of Equation 5 in Equation 4 resulted in a general empirical equation showing M as a function of C and t :

$$M = 20 (185 - t) C^{-0.29} \quad (6)$$

The third and fourth columns of Table IV show the degree of accuracy with which Equation 6 reproduces the values of M from which it was derived.

Equation 6 may be used to calculate values of M which, in turn, may be substituted in Equation 2 for the calculation of equilibrium relationships. The necessity of using two separate equations may be avoided by combining Equation 6 with Equation 2. Equation 7, which results from this procedure, is a general equation showing the equilibrium relationships between X , C , S , P , and t :

$$\frac{X^2 C^{1.29}}{SP (1 - X)(185 - t)} = 10 \quad (7)$$

Equation 7 may be used to calculate equilibrium relationships for any values of C and t within the range of the experimental work (from about 20° to 70° C. and from about 0.5 to 2.0 normal in sodium).

USE OF EQUATION 7

There are two questions which Equation 7 is apt to be called upon to answer. One asks what will be the partial pressure of carbon dioxide in a gas phase which is in equilibrium, at a specified temperature, with a sodium carbonate-bicarbonate solution of specified total sodium concentration and having a specified fraction of the sodium in the form of the bicarbonate. The second question asks what fraction of the sodium will be in the form of the bicarbonate in a solution which has a specified total sodium concentration and which is in equilibrium, at a specified temperature, with a specified partial pressure of carbon dioxide in the gas phase. Two typical examples will illustrate how Equation 7 answers these questions:

EXAMPLE 1. A gas mixture containing 18 per cent carbon dioxide (wet basis) is to be treated to remove part of the carbon dioxide. The total pressure is to be 1.0 atmosphere; the temperature, 35° C. The liquor which is to absorb the carbon dioxide is to be a sodium carbonate-bicarbonate lye in which the sodium concentration is 1.8 normal and in which 55 per cent of the sodium is in the form of the bicarbonate. It is desired to determine how low the carbon dioxide content of the gas can be reduced by this treatment.

SOLUTION. The carbon dioxide content of the gas can be reduced until the partial pressure of carbon dioxide in the gas becomes equal to the equilibrium partial pressure of carbon dioxide exerted by the liquor. By substituting the values given below in Equation 7, the equilibrium partial pressure of carbon dioxide exerted by the liquor may be calculated:

$$\begin{aligned} C &= 1.80 \\ X &= 0.55 \\ t &= 35 \\ S &= 0.0262 \\ P &= \frac{(0.55)^2(1.80)^{1.29}}{(10)(0.0262)(0.45)(185 - 35)} = 0.0364 \text{ atm.} \end{aligned}$$

The partial pressure of carbon dioxide in the gas phase can be reduced to 0.0364 atmosphere, or, in other words, the carbon dioxide content of the gas can be reduced to 3.64 per cent (wet basis).

EXAMPLE 2. A sodium carbonate-bicarbonate lye in which the sodium normality is 1.9 and in which, at the start, half of the sodium is in the form of the bicarbonate, is to be brought to equilibrium with a gas containing 16 per cent carbon dioxide (dry basis). The total pressure is to be 1.0 atmosphere; the temperature, 45° C. What fraction of the sodium will be in the form of the bicarbonate at equilibrium?

SOLUTION. The solution is merely a matter of substitut-

ing values of C , t , S , and P in Equation 7 and solving for the value of X .

$$\begin{aligned}C &= 1.9 \\t &= 45 \\S &= 0.0215 \\P &= \frac{(760 - 71)(0.16)}{(760)} = 0.145 \text{ atm.}\end{aligned}$$

Vapor pressure of water at 45° C. = 71 mm.
Substituting in Equation 7,

$$\frac{X^2(1.9)^{1.29}}{(0.0215)(0.145)(1 - X)(185 - 45)} = 10$$

$$X = 0.725$$

When the system reaches equilibrium, the sodium in the form of the bicarbonate will amount to 0.725 of the total sodium.

For convenience in using Equation 7, a number of values of S (based on the measurements of Bohr, Geffcken, and Just, as reported by Seidell) are presented in Table V.

TABLE V. SOLUBILITY OF CARBON DIOXIDE IN WATER

t	S	t	S	t	S
15	0.0455	45	0.0215	75	0.0120
25	0.0336	55	0.0175	85	0.0090
35	0.0262	63	0.0151	100	0.0065

NOMENCLATURE

- B = a numerical coefficient, defined by Equation 5
 C = total sodium concentration, normality
 M = a numerical coefficient, defined by Equation 2
 P = partial pressure, atm.
 p = partial pressure, mm.
 S = solubility of CO_2 in water, gram-moles/liter at 1 atm. partial pressure
 t = temperature, °C.
 X = fraction of sodium in form of bicarbonate
 1 - X = fraction of sodium in form of carbonate

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Absorption of Carbon Dioxide in Aqueous Sodium Carbonate-Bicarbonate Solutions

II. Rate of Absorption

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Working with solutions from 1 to 2 normal in sodium over a temperature range 25° to 63° C. in a wetted-wall absorption tower, 2.54 cm. i. d. by 152 cm. long, it is found that the coefficient of absorption, K_g , is independent of sodium concentration, decreases approximately 40 per cent with increasing bicarbonate normality from 0.2 to 0.6, and doubles with a temperature rise of approximately 22° C. over the same bicarbonate normality range.

FOR both the theoretical consideration and the practical application of a process of gas absorption, such as the absorption of carbon dioxide into sodium carbonate-bicarbonate solutions, it is desirable to know:

(1) How much of the solutum can be transferred from the carrier to the extractor? [The nomenclature used here is that suggested by Lewis (6). The material being absorbed is the solutum; the inert gas which introduces the solutum into the system is the carrier; the liquid into which the solutum is absorbed is the extractor.]

(2) How rapidly can the solutum be transferred from carrier to extractor?

An attempt has been made to answer these questions for the absorption of carbon dioxide into sodium carbonate-bicarbonate solutions for conditions approximating those under

which this absorption process is applied industrially for the recovery of carbon dioxide from flue gas. The first question involves equilibrium relationships; the equilibrium between carbon dioxide and sodium carbonate-bicarbonate solutions has been considered in Part I of this series (4). The second question involves absorption rate.

The mechanism of the absorption process for a system in which the solutum reacts chemically with the extractor is not well understood. Until an adequate theory shall be developed, experimental results are best presented by giving values of an absorption rate coefficient for the various conditions investigated. The over-all absorption coefficients, K_G and K_Ga , are defined by Equations 1 and 2:

$$K_G = \frac{\frac{dW}{d\theta}}{A \Delta P_{av.}} \quad (1)$$

$$K_Ga = \frac{\frac{dW}{d\theta}}{V \Delta P_{av.}} \quad (2)$$

where $dW/d\theta$ = absorption rate (weight per unit of time)
 A = interfacial area through which given absorption takes place
 V = volume of tower in which given absorption takes place
 $a = A/V$ = interfacial area per unit of tower volume
 $P_{av.}$ = mean driving force (pressure)¹

Earlier workers have investigated the influence upon absorption rate of various changes in operating conditions. The writers have investigated the influence of temperature and chemical composition of the liquor upon absorption rate.

There are reported results which indicate a relationship of direct proportionality between $dW/d\theta$ and $\Delta P_{av.}$ The investigations of Byrne and Carlson (1), Payne and Dodge (8), and Riou (9) indicate this direct proportionality for the absorption of carbon dioxide in sodium carbonate-bicarbonate solutions. Williamson and Mathews (13) and Sieverts and Fritzsche (10) report measurements of absorption rate for carbon dioxide in potassium carbonate-bicarbonate solutions; Monaweck and Baker (7) and Cantelo, Simmons, Giles, and Brill (2) have investigated the absorption of carbon dioxide in water. The direct proportionality, indicated in the reported data of all these investigations, apparently has abundant experimental verification.

Rate of absorption has been found to be quite sensitive to changes in liquor flow rate but essentially independent of

¹ $\Delta P_{av.}$ may sometimes be a simple arithmetic average, sometimes a logarithmic mean, and sometimes a mean value which is obtainable only by graphical integration; the particular mean to be used is determined by the characteristics of the system and the degree of accuracy demanded by the problem being considered. In the present paper $\Delta P_{av.}$ is a logarithmic mean of the driving forces at the terminals of the absorption tower. For further discussion of mean driving forces refer to Walker, Lewis, and McAdams (11).

CARBON DIOXIDE
COMPRESSORS



*Courtesy Dry Ice Division
Michigan Alkali Co.*

gas flow rate. Payne and Dodge (8) found that a fourfold increase in gas flow rate had no effect, but that an increase in liquor flow rate materially increased K_G . Byrne and Carlson (1) and Riou (9) also investigated the relationships between gas and liquor flow rates and rate of absorption; the results reported by these investigators are in good agreement with the findings of Payne and Dodge. The evidence indicates that agitation of the gas phase has little effect, while agitation of the liquid phase exerts a decided influence on absorption rate.

Payne and Dodge, Byrne and Carlson, and Riou all report that increase in temperature causes a marked increase in the absorption rate coefficient. The present authors' experimental investigation of the relationship between the coefficient and temperature confirms the findings of these earlier investigators.

The influence of the chemical composition of the liquor on the absorption rate coefficient has been investigated by several workers. The coefficient has usually been found to be little influenced by sodium concentration but quite sensitive to the carbonate-bicarbonate ratio. Payne and Dodge observed these effects, as did Williamson and Mathews in their experiments with potassium carbonate-bicarbonate solutions. The present authors have made a study of the relationship between the chemical composition of the liquor and the absorption rate coefficient; the results of this study are presented in graphical form in Figure 3.

APPARATUS AND EXPERIMENTAL METHOD

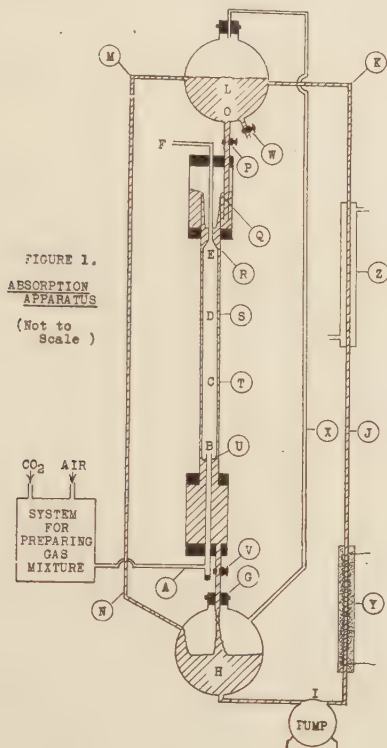
Measurements of absorption rate were made in a counter-current, wetted-wall absorption tower, similar to those described by Haslam, Hershey, and Keen (5) and by Grenewalt (3). The outstanding advantage of this type of apparatus is that it provides a gas-liquid interface of definite and measurable area.

Figure 1 shows the absorption tower and liquor recirculation system, and reveals how the liquor and gas streams flow through the absorption system:

The gas stream was adjusted in auxiliary apparatus before it was passed into the system shown in Figure 1. Adjustment involved regulation of temperature, humidity (which was always maintained at 100 per cent saturation), rate of flow, and ratio of carbon dioxide to air. The gas stream, adjusted as desired, entered the absorption system at *A*, passed into the contact tube at *B*, flowed upward passing *C* and *D*, entered the inverted funnel at *E*, and escaped to the atmosphere at *F*.

The liquor was introduced into the system before the run started by removing stopper *G* and pouring the liquor into flask *H*. Pump *I* circulated the liquor around the circuit, *JKL MN*, and back to flask *H*. The liquor did not come into contact with the gas stream during this part of the circuit. A stream of liquor bled from overhead flask *L*, through outlet *O*, was fed to the contact tower. Valve *P* controlled the flow of liquor to the tower. Liquor flowed into the top of the contact tube at *Q* and was distributed on to the inner wall of the tube by the inverted

funnel at *R*. Liquor and gas streams first came into contact with each other at the point where the liquor emerged from behind the inverted funnel. Liquor flowed down the inner wall of the contact tube, passing *S* and *T*, in contact with the gas stream which was rising upward through the center of the contact tube. A liquor seal, maintained at *U*, prevented gas from escaping downward. Liquor passed through valve *V* and returned to flask *H*. Cock *W* provided a place where samples of the liquor could be withdrawn. *X*, a vent line between the upper and lower flasks, was necessary to permit the liquor to flow down the tower wall smoothly. Heater *Y* and cooler *Z* were used to control the temperature of the liquor stream; there were thermometers (not shown in Figure 1) which indicated liquor temperature.



Dimensions of the feed and discharge flasks and the contact tube will indicate the size of the absorption apparatus. The upper (feed) flask and the lower (discharge) flask were 1.5- and 2-liter, round-bottom Pyrex flasks, respectively. The contact tube was a glass tube having an inside diameter of 0.94 inch (2.39 cm.) and a total length of 60 inches (152 cm.); the length used for absorption was the distance from *R* to *U*, which was 50 inches (127 cm.); the area of gas-liquid interface was essentially the area of the inside wall of the tube between points *R* and *U*, which was 148 square inches (953 sq. cm.).

The procedure followed in using the apparatus was as follows:

For each run a solution having the desired concentration with respect to hydroxide, carbonate, bicarbonate, and sodium was prepared by mixing appropriate volumes of standard solutions of sodium hydroxide, sodium carbonate, and sodium bicarbonate.

A measured volume of solution (usually 2500 cc.) was poured into the lower flask. The circulation pump was running and the valve between the overhead flask and the contact tower was shut while the liquor was being introduced.

The liquor stream was regulated with respect to temperature and rate of flow through the tower. The liquor heater and cooler (Figure 1) provided control of temperature. Rate of flow through the tower was regulated by tower feed valve *P*. A dial on this valve made it possible to obtain approximately the desired flow rate with the initial setting of the valve; final adjustment was made by trial. Flow rate was determined by closing valve *V* and timing, with a stop watch, the rise of the liquor level in the enlarged section at the base of the tower.

The gas stream was regulated with respect to temperature, humidity, flow rate, and composition. While these adjustments in gas stream conditions were being made, the gas stream was by-passed around the contact tower. Temperature was regulated by passing the gas through coils in a bath of heated water. Regulation of flow rate and gas composition was accomplished by adjusting valves on the carbon dioxide and air feed lines; flowmeters, checked by analysis of the mixed gas, facilitated accurate control. Humidification to 100 per cent saturation was accomplished by passing the gas through water, which had been acidified and saturated with carbon dioxide at the partial pressure of the carbon dioxide in the gas stream.

The gas stream was switched from the by-pass to the contact tower, and the flow rates of both streams were readjusted.

Liquor samples were taken at convenient time intervals (1 or 2 minutes when absorption was rapid; 5, 10, 15, or 20 minutes when absorption was relatively slow). Sampling started as soon as gas and liquor streams had been brought together and regulated satisfactorily, and continued until the liquor composition had changed through the range over which absorption rates were to be measured. The gas mixture fed to the tower was sampled and analyzed several times in the course of each run.

The barometric pressure was observed and recorded; the pressure in the contact tower (above barometric) was also observed and recorded.

When the liquor composition had changed through the desired range, the rate of liquor flow was rechecked. This concluded the run, and operation of the apparatus was stopped.

All liquor samples were analyzed for sodium, carbonate, and bicarbonate concentrations. (Analysis was accomplished by a modification of the Winkler method; this modification was described in the first paper of this series, 4).

RESULTS OF EXPERIMENTS

Significant items from the data sheet (Table I) of a typical run illustrate the sort of information obtained in this series of experiments.

Preliminary to obtaining a series of values of K_G for the conditions under which a given run was made, values of absorption rate, $dW/d\theta$, and mean driving force, $\Delta P_{av.}$, must be obtained from the information carried on the data

sheet. Having obtained values of $dW/d\Theta$ and $\Delta P_{av.}$ for any instant during the run, these values may be substituted in Equation 1, along with the known value of A (953 sq. cm.) and the corresponding values of K_G determined.

TABLE I. DATA SHEET OF RUN F-3

(Date, 6-12-31; barometer, 738 mm. of mercury)

Liquor:	
Initial volume, cc.	2500 $\pm$ 25
Sodium normality	1.03 $\pm$ 0.01
Temperature, ° C.	63 $\pm$ 1
Flow rate through tower, cc./min.	960 $\pm$ 20
Volume of sample, cc.	35
Gas:	
Pressure in tower, mm. of Hg	753 $\pm$ 2
Temperature, ° C.	63 $\pm$ 1
Composition (Orsat at 25° C.), % CO ₂	19.1
Flow rates, cc./min.: ^a	
Dry CO ₂	2400 $\pm$ 150
Dry air	9600 $\pm$ 600
Total dry gas	12,000 $\pm$ 600

SUMMARY OF INFORMATION OBTAINED FROM ANALYSIS OF LIQUOR SAMPLES

1b	2c	3d	4e	5f
Minutes	Liters	Grams	Grams	Normality
0			0	0.07
5	2.465	1.882	1.882	0.116
10	2.430	1.170	3.052	0.138
15	2.395	1.462	4.514	0.166
20	2.360	1.661	6.175	0.198
30	2.325	2.185	8.360	0.241
40	2.290	2.150	10.510	0.284
50	2.255	1.932	12.442	0.322
55	2.220	0.755	13.197	0.338
60	2.185	0.821	14.018	0.355

^a Flow rates show volumes of dry gas for 0° C. and 760 mm. mercury.

^b Time at which the sample was withdrawn (after the initial sample).

^c Volume of liquor in the absorption apparatus between any two successive samples.

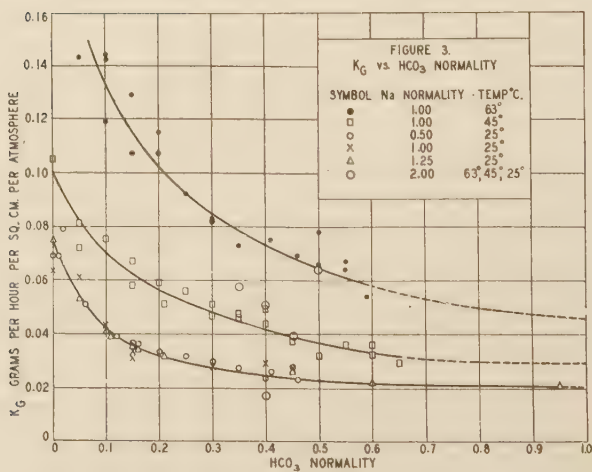
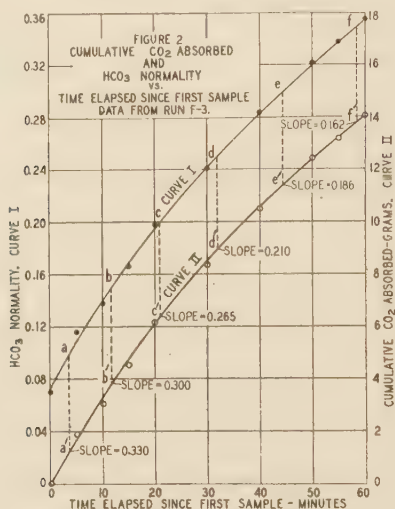
^d Carbon dioxide absorbed by the liquor which was in the apparatus between two successive samples.

^e Cumulative addition of the values given in column 3. Column 4 shows how much carbon dioxide had been absorbed in the time interval between the initial sample and any other sample.

^f Bicarbonate normality of any liquor sample. In this expression of concentration no consideration is given to ionization. A solution in which the sodium normality is 1.03 and the bicarbonate normality is 0.241 is the solution which would be prepared by dissolving $0.241 \times 84 = 20.25$ grams of sodium bicarbonate and $(1.03 - 0.241) \times 53 = 41.9$ grams of sodium carbonate in enough water to make one liter of solution.

Values of absorption rate, $dW/d\Theta$, corresponding to various values of bicarbonate normality were obtained by graphical treatment of data sheet items. Figure 2 is a graph of certain items from the data sheet of run F-3. Curve I shows bicarbonate normality (column 5 on data sheet) plotted against time elapsed since first sample (column 1 of data sheet). Curve II shows cumulative carbon dioxide absorbed (column 4 of data sheet) vs. time elapsed since first sample. The slope of curve II at any point gives the rate at which carbon dioxide was being absorbed at the instant corresponding to that point. Convenient values of bicarbonate normality were selected on curve I (such as the values corresponding

to points, *a*, *b*, *c*, etc.); the corresponding absorption rates were obtained from curve II (by determining the slope of curve II at points *a'*, *b'*, *c'*, etc., by graphical differentiation). All of the experimental data were treated in this manner to yield corresponding values of bicarbonate normality and absorption rate.



For each pair of corresponding values of bicarbonate normality and absorption rate, the mean driving force, $\Delta P_{av.}$, was calculated. This calculation required a knowledge of the partial pressure of carbon dioxide in the gas stream at the bottom and at the top of the tower, and a knowledge of the equilibrium pressure of carbon dioxide exerted by the

liquor at the bottom and top of the tower. Partial pressure of carbon dioxide in the gas stream was calculated from data supplied by Orsat analyses, used in conjunction with the known total pressure. The pressure of carbon dioxide in equilibrium with various liquor compositions was calculated by the method described in Part I of this series (4). The driving force, ΔP , for any level in the tower, is the difference between the partial pressure of carbon dioxide in the gas stream and the equilibrium pressure of carbon dioxide exerted by the main body of the liquor at the given level. The mean (over-all) driving force, $\Delta P_{av.}$, is the logarithmic mean between the values of ΔP at the top and bottom of the tower.

Substitution of $dW/d\theta$, $\Delta P_{av.}$, and A in Equation 1 will yield values of K_G . Any units of weight, time, pressure, and area might conceivably be used. Unfortunately, the literature carries almost as many different sets of units as there are articles concerning absorption rate. The units for K_G in this paper will be grams per hour per atmosphere per square centimeter. [These units were selected because they are consistent with the units selected by Payne and Dodge (8) in a recent article.] To convert K_G in these units to the corresponding coefficient in units of pounds per minute per atmosphere per square foot, multiply by 0.0341. Calculation of K_G for the instant during run F-3 when the bicarbonate normality was 0.15 illustrates the procedure followed. The bicarbonate normality was 0.15 twelve minutes after the first sample was taken (point *b* on curve I of Figure 2); at this instant carbon dioxide was being absorbed at a rate of 0.30 gram per minute (slope of curve II at point *b'*); the mean driving force, $\Delta P_{av.}$, at this instant, was 0.146 atmosphere (calculated from data sheet information); the interfacial area (a constant of the apparatus) was 953 sq. cm. Substituting these values in Equation 1 and multiplying by 60 to convert the absorption rate from grams per minute to grams per hour:

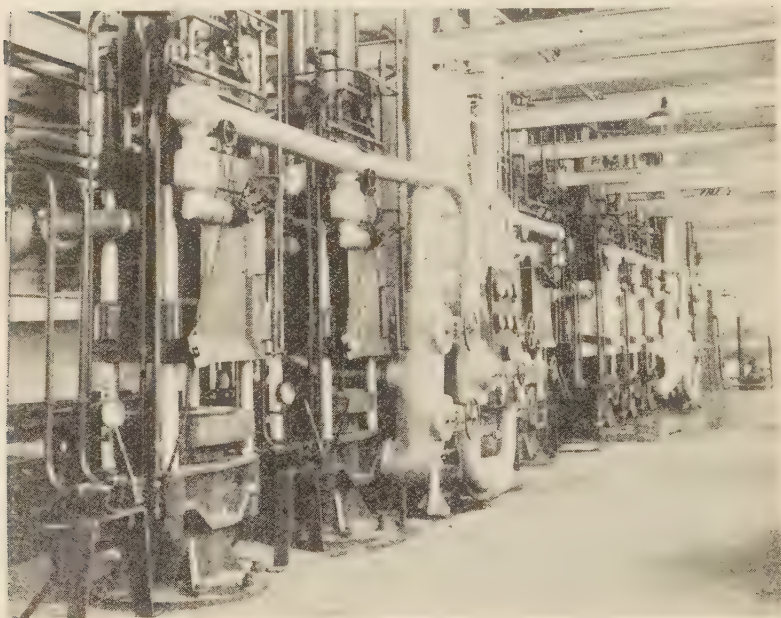
$$K_G = \frac{60 \times 0.30}{953 \times 0.146} = 0.129$$

The summarized results of a number of experiments in which carbon dioxide was absorbed in sodium carbonate-bicarbonate solutions are presented in Figure 3. Absorption rate and K_G are shown for various conditions of temperature, sodium concentration, and bicarbonate concentration. In these experiments, the partial pressure of carbon dioxide in the gas phase varied from 0.136 to 0.193 atmosphere, the pressure of carbon dioxide from the liquid from 0 to 0.09 atmosphere, and the driving force (ΔP) from 0.09 to 0.18 atmosphere.

DISCUSSION OF RESULTS

Figure 3 reveals that:

The coefficient K_G is independent of sodium concentration. This is shown by the results of experiments at 25° C. which include runs for sodium normalities of 0.5, 1.0, and 1.25, and one run in which the sodium normality was 2.0; with the exception of the point for 2.0 *N* sodium, the points for the different sodium normalities all fall on the same curve (within the experimental error). The experimental evidence indicates that K_G is independent of sodium concentration for sodium normalities up to 1.25; the experiments for a sodium normality of 2.0 were particularly difficult to perform and undoubtedly carry a relatively great experimental error; three of the five points for a sodium normality of 2.0 (two points at 45° and one at 25° C.) are comparatively far from the curves based on points for lower sodium concentrations, but, considering that two points do hit the curves and that "wild" points occur both above and below the corresponding curves, there is some justification for concluding that



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PRESSES IN WHICH COMPRESSED CARBON DIOXIDE IS EXPANDED TO FORM A CAKE OF DRY ICE

K_G is independent of sodium concentration for concentrations up to 2.0 *N* sodium.

K_G decreases with increasing bicarbonate concentration; the rate of decrease is more rapid for low than for high bicarbonate concentrations. The three curves (for 25°, 45°, and 63° C.) are of similar shape; each falls rapidly at first and then gradually flattens out as K_G approaches a constant value.

K_G increases with increasing temperature. Between bicarbonate normalities of 0.2 and 0.6, K_G doubles with a temperature rise of about 22° C. Whitman and Davis (12), who investigated the absorption of carbon dioxide in sodium carbonate solution in a bubble-cap tower, found that the coefficient doubled for every 24° C. rise of temperature.

Information such as is presented in Figure 3 should prove

useful for determining the relationship between the capacity of a given absorption apparatus and the conditions (of temperature and liquor composition) under which the apparatus is to operate. A rearrangement of Equation 1 shows that the capacity of a given apparatus, $dW/d\theta$, is proportional to the product of interfacial area, A , absorption rate coefficient, K_G , and mean driving force, ΔP_{av} :

$$dW/d\theta = AK_G\Delta P_{av}. \quad (1)$$

The present series of papers has not considered the relationship between operating conditions (of temperature and liquor composition) and A ,² but Part I (4) has presented information which permits calculation of ΔP_{av} , and this present paper furnishes information (Figure 3), which gives K_G for various conditions of temperature and liquor composition. For various operating conditions under which the value of A is essentially constant, the product $K_G\Delta P_{av}$ is proportional to and may be used as a measure of the capacity of the apparatus.

The choice of an optimum bicarbonate normality for the absorption process of carbon dioxide purification cannot be determined from the standpoint of absorption alone but requires consideration of both the absorption process (which has been discussed in this paper) and the boil-off process by which the carbon dioxide is recovered from the carbonate-bicarbonate solution. (The boil-off process is beyond the scope of the present paper.) Low bicarbonate normality permits high capacity for apparatus on the absorption side of the cycle but low capacity for apparatus on the boil-off side; high bicarbonate normality reverses the situation. An intelligent selection of an optimum bicarbonate normality can be made only by balancing these opposite tendencies to find the bicarbonate normality at which the capacity of the whole cycle (absorption and boil-off) will be maximum.

The absorption rate coefficient, K_G , and the mean driving force, ΔP_{av} , for the absorption of carbon dioxide in sodium carbonate-bicarbonate solutions, vary with temperature and with bicarbonate normality in such a way that, for any apparatus which is to perform a given absorption task, there is a particular combination of temperature and range of bicarbonate normalities which will permit maximum capacity. The information furnished by the experimental work described in this paper should help one to select the optimum conditions of temperature and bicarbonate normality for an apparatus which is to operate within the range of conditions considered in this paper.

² Interfacial area, A , is essentially a function of the design of the apparatus although it may vary somewhat with the rate at which gas and liquor streams flow through the apparatus; the influence of temperature and liquor composition upon A is indirect and, in a packed tower, is noticeable only when changes in liquor viscosity (resulting from changes in temperature and chemical composition) cause the tower packing to be more or less completely wetted.

In considering absorption where the liquor composition (bicarbonate normality) changes throughout the apparatus, a logarithmic mean driving force, such as used for the work described here, may sometimes lead to serious error. It may be demonstrated (6) that the logarithmic mean is justified when (as in the experiments of the research described here) the apparatus is so short or the volume of liquor used so large that liquor composition changes only slightly throughout the apparatus, and, consequently, the equilibrium pressure of carbon dioxide exerted by the liquor is essentially constant. When the equilibrium pressure of carbon dioxide exerted by the liquor changes throughout the apparatus, the use of the logarithmic mean driving force is justified only if the equilibrium pressure is directly proportional to the amount of carbon dioxide which has been absorbed by the liquor (Henry's law). For the absorption of carbon dioxide in carbonate-bicarbonate solutions Henry's law does not hold, and use of a logarithmic mean will yield a result which may be more or less in error. When the change (throughout the apparatus) in the equilibrium pressure of carbon dioxide exerted by the liquor is small compared to the least value of ΔP in the apparatus, use of the logarithmic mean will yield results which are sufficiently accurate for most engineering purposes; when the change in equilibrium pressure is appreciable (of the same order of magnitude or greater) compared to the least value of ΔP , use of the logarithmic mean may introduce an error which is too large to be tolerated. Whenever the logarithmic mean is not sufficiently accurate, the mean driving force may be determined by methods of graphical integration which are beyond the scope of the present paper but which may be worked out by application of principles set forth by Walker, Lewis, and McAdams (11).

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